

**THE PHYSICAL NATURE AND THE CHEMICAL REACTIVITY
OF A
HETEROGENEOUS MgO/VERMICULITE FLUE-GAS SORBENT**

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INTRODUCTION

Many advancing new technologies for removing SO_2 and NO_x from flue gas emissions involve dry scrubbing, in contrast to wet scrubbing, the most widely used technology today [1]. These developments are being encouraged by a real need to reduce costs, to increase overall efficiency, and to avoid major problems relating to water pollution and to sludge handling and disposal. Cost reductions and increased efficiency can be achieved by using regenerable, high-capacity sorbents, and the water and waste-disposal problems can be alleviated by handling sorbents dry and by generating useful by-products from the wastes produced. Recently, a new family of dry, regenerable sorbents, called NelSorbents, has reached the stage of pilot-scale testing.

The reactivity of unsupported MgO for removal of flue-gas components has been studied extensively [2]. Studies have also been done on inert supports for MgO and other oxides [3]. In addition, the reactivity and catalytic activity of such support-type materials as aluminates, silicates, and zeolites, have been studied [4].

The present study was undertaken to determine the physical nature and the chemical reactivity of a promising NelSorbent material having vermiculite as a support for hydrated MgO. This patented sorbent has been shown to effectively remove SO_2 and NO_x from flue gases in the laboratory and in pilot-scale operations. A fundamental scientific investigation of the material was performed to improve current methods of preparation, conditioning, utilization, and regeneration.

EXPERIMENTAL

NelSorbent Preparation

The NelSorbent used in the studies was prepared by Sanitech, Inc. using the techniques described in U.S. Patent Number 4,721,582. Vermiculite was variously coated with several grades of MgO, $\text{Mg}(\text{OH})_2$, or MgCO_3 . The samples were both bench- and batch-processed at 45% by weight MgO and conditioned at temperatures of 400, 550, and 800°C.

Sample Preparation

Sanitech exposed NelSorbents both in a dry and in a moistened condition to side-streams of flue-gas at the Gorge Power Plant of Ohio Edison in Akron, Ohio. In the laboratory, vermiculite and NelSorbents were exposed to synthetic flue-gas mixtures and to SO_2 or NO_x under varying relative humidities.

NelSorbent Regeneration

Flue-gas exposed samples were regenerated at 800°C in either air or in a 40% CH₄/60% N₂ mixture.

Gas Adsorption

Nitrogen adsorption and desorption measurements were made in a classical gas adsorption apparatus at liquid nitrogen temperature. Pressures were measured with a mercury manometer and masses were measured to ±0.01 milligrams with a Cahn electromagnetic balance. Adsorption and desorption for SO₂ and NO_x, both in the presence and in the absence of added moisture, were measured to ±0.2 milligrams with a quartz spring balance.

Water adsorption isotherms were carried out over a period of weeks. Samples in desiccators were exposed to specific relative humidities achieved by various saturated salt solutions. Weight gains in these trials were determined with an analytical balance.

Infrared Spectra

Fourier transform infrared spectra (FTIR) were measured with an IBM model 32 spectrophotometer. Both powder samples in a nitrogen atmosphere and solution spectra in silver chloride cells were measured. A Spectra-Tech high temperature environmental chamber was used to run series of spectra at elevated temperatures.

X-Ray Diffraction

Samples were packed in Lindeman glass capillaries and exposed to Cu radiation at 35 kilovolts and 15 milliamps for about seven hours. The interlayer spacings were calculated from the resultant powder patterns.

Electron Micrographs

Electron micrographs were made with several microscopes. Due to static charge phenomena, the best results were obtained at very low amperages and gave good resolution to the nanometer range.

RESULTS AND DISCUSSION

Nitrogen Isotherms

The classical BET theory was used to analyze adsorption isotherms such as those shown in Figures 1 and 3. Moisture variability is a problem in establishing a reliable mass baseline for minerals such as vermiculite. To minimize this variability, the samples were outgassed under a vacuum as the sample was heated to 200°C. Although this procedure reduced the baseline variability, it was necessary to plot the data in the form shown in Figures 2 and 4 to get reproducible results.

For the N(1-X) ordinate of Figures 2 and 4, N represents the mass reading in milligrams obtained from the Cahn balance. When X=P/Po=0, the intercept gives the correct baseline. Adding the baseline to the slope of the plot gives the mass in milligrams for a monolayer by the BET theory.

Surface Areas

BET surface areas with N_2 are shown in Table 1. The value of 4 M^2 /gram represents the external surface area of vermiculite.

TABLE 1
BET SURFACE AREAS - M^2 /gram Sample

<u>SAMPLE</u>	<u>TEMPERATURE</u>	<u>NITROGEN</u>	<u>WATER</u>
Conditioned:			
Vermiculite	550°C	4	
MgO	550°C	50	
NelSorbent-Bench	550°C	55	270
NelSorbent-Bench	800°C	11	
NelSorbent-Batch	550°C	16	52
Regenerated NelSorbents:			
Batch-Air	800°C	12	57
Batch- CH_4/N_2	800°C	8	
Previous Sample in Air	500°C	2	45

The surface area of MgO varies considerably depending on how it is prepared [7,8]. The NelSorbent bench-processed at 550°C had a surface area of 55 M^2 /gram of sample. Since this NelSorbent is only 45% MgO by weight, this corresponds to a surface area for this MgO of over 100 M^2 /gram or more than twice that of the original MgO. Special treatment of MgO has been shown to give areas in excess of 500 M^2 /gram [9].

Exposure to high temperatures caused surface areas to drop. Surface areas of NelSorbent conditioned at 800°C and NelSorbent batch-processed at 550°C, where hot-spots may exist, dropped below 20 M^2 /gram. After gas exposure, the batch-processed NelSorbents were regenerated and the surface areas dropped even more, to 12 and 8 M^2 /gram. The sample regenerated in a CH_4/N_2 atmosphere had a grey color which disappeared on heating in air to 500°C. However, the surface area then dropped even more to 2 M^2 /gram. The grey colored sample gave a positive sulfide test with lead acetate paper.

The 550°C bench-processed NelSorbent was sieved into fractions >1400, 500-1400, 250-500, and <250 microns. The surface areas ranged from 23-36 M^2 /gram sample, considerably below the 55 M^2 /gram for the unsieved sample. In the unsieved sample, the larger vermiculite particles may protect the MgO from being sintered.

Water Isotherms

Table 1 also shows the surface areas determined by the adsorption of water on four selected samples. These water areas exceed the nitrogen areas by greater than three-fold. The most dramatic effect was for the regenerated sample which went from 2 to 45 M^2 /gram. This shows that the conditioning water can penetrate the interlayers of the vermiculite even if external surface area has been previously reduced.

NO_x Adsorption

Table 2 shows that a NelSorbent conditioned at 550°C and exposed to NO_x under ambient conditions had an 11.2% weight gain which was retained on evacuating the system. After heating to 200°C in vacuum, the weight gain dropped to 7.0%. Vermiculite on the other hand, gained only 2.2%

by weight NO_x under similar conditions and lost almost all of the weight by pumping in a vacuum without the addition of heat. Hence, there is a much stronger interaction of NO_x with the NelSorbent than with the vermiculite, the former being akin to chemical adsorption and the latter to physical adsorption.

TABLE 2
 NO_x/SO_2 ADSORPTION - PERCENTAGE WEIGHT GAIN

SAMPLE	AMBIENT	VACUUM	
	EQUILIBRIUM	20°C	200°C
NO_x ADSORPTION			
550°C NelSorbent ^a	11.4%	11.4%	7.0%
Vermiculite ^a	2.2%	0.3%	--
SO_2 ADSORPTION			
550°C NelSorbent ^b	4.0%	--	--
Vermiculite ^a	1.0%	0.5%	--
550°C NelSorbent ^a	4.5%	3.4%	--
550°C NelSorbent ^c	94% ^d	57%	30%
Vermiculite ^c	24% ^e	2%	--

a. Prepared at ambient conditions b. Prepared by pumping to vacuum
c. Prepared at 100% relative humidity d. Weight gain includes 37% water e. Weight gain includes 12% water

SO_2 Adsorption

NelSorbent conditioned at 550°C gained nearly 5% by weight when exposed to SO_2 under ambient conditions and dropped a few percent when pumped down in a vacuum. However, when the NelSorbent was pre-conditioned for a week in 100% relative humidity, there was over a 50% weight gain of SO_2 which remained on evacuating the system under ambient conditions. Even on heating to 200°C in a vacuum, 30% by weight SO_2 remained indicating a strong chemical interaction.

Vermiculite gained little weight under ambient conditions when exposed to SO_2 and the weight gain dropped to near the original sample weight when pumped to a vacuum under ambient conditions. Although there was a larger weight gain when the vermiculite was first saturated with water vapor for a week at 100% relative humidity, most of the weight gain was lost on pumping to a vacuum. This suggests a very weak physical interaction between SO_2 and vermiculite even in the presence of a large amount of pre-absorbed water.

FTIR Solid Spectra

Raw vermiculite and 550°C conditioned vermiculite gave bands at 3000-3500 cm^{-1} and at 1650 cm^{-1} . Silicon-oxygen absorption near 1000 cm^{-1} interfered with sulfite and sulfate analyses.

Conditioned NelSorbent gave a strong $\text{Mg}(\text{OH})_2$ band at 3700 cm^{-1} which disappeared as the temperature of conditioning was increased. MgCO_3 peaks at 1500 cm^{-1} and 850 cm^{-1} became evident on heating as well as 1400 and 400-700 cm^{-1} peaks for MgO . Batch-processed material did not as effectively reduce the $\text{Mg}(\text{OH})_2$ peaks as did bench-processing. When MgCO_3 was used as the starting material, the carbonate peaks remained strong even after conditioning indicating that insufficient energy was added to the system to break down the carbonate.

When the NelSorbent was exposed to SO_2 , a sulfite peak at 950 cm^{-1} , a sulfate peak at 1100 cm^{-1} , and bisulfite/bisulfate peaks at 2250 cm^{-1} were noted in addition to the previously discussed peaks and bands. MgCO_3 was particularly dominant when NelSorbents were run under dry conditions at the power plant suggesting that CO_2 strongly competes in adsorption under these conditions.

In general, the concentration of NO_x was not high enough in the flue-gas streams to be absorbed to such an extent to be detected by FTIR. One NelSorbent sample exposed to NO and superheated steam showed the presence of nitrite at 1250 cm^{-1} .

The spent NelSorbents regenerated in air showed MgO , MgCO_3 , and MgSO_4 peaks. The sample regenerated in CH_4/N_2 suggested the presence of magnesium compounds not previously seen in other samples, perhaps Mg or MgS . Subsequent heating of the sample in air eliminated these compounds and peaks were observed for MgO and MgSO_4 . Also, a particularly large MgCO_3 peak appeared which may have been previously masked.

A NelSorbent well-spent with flue-gas was heated in situ in the FTIR environmental chamber. The sample was mixed with KBr and heated in a stream of nitrogen. Bisulfite/bisulfate peaks disappeared by 200°C , water peaks reached a minimum at 300°C , MgO and MgCO_3 disappeared by 500°C , and MgSO_4 increased in intensity at 400°C and remained constant up to 660°C , the maximum temperature of analysis.

FTIR Solution Spectra

Aqueous extracts of NelSorbents spent with flue-gas indicated the sulfate ion at 1100 cm^{-1} . No sulfite was detected, perhaps due to its oxidation to sulfate.

A NelSorbent sample saturated in the laboratory with moisture and with NO_x gave a nitrite peak at 1240 cm^{-1} . The nitrate peak was absent.

Basal Plane X-Ray Spacings

The raw and the 550°C processed vermiculite gave a 14 angstrom interlayer spacing expected for two layers of water. When conditioned at 550°C for 30 minutes in the NelSorbent preparation, the interlayer distance dropped to 12 angstroms expected for one interlayer of water. When conditioned at 800°C for 30 minutes, the interlayer collapsed to a 9 angstrom distance which indicates the complete loss of interlayer water.

The interlayer distance expanded back to 14 angstroms for the NelSorbent in the flue-gas stream indicating the presence of enough water to re-expand the lattice.

Interplanar X-Ray Spacings

Table 3 shows interlayer distances and compound assignments found for a NelSorbent which was used at the power plant during a week of heavy rains.

TABLE 3
NELSORBENT EXPOSED TO FLUE GAS

<u>COMPOUND</u>	<u>ANGSTROMS</u>	<u>COMPOUND</u>	<u>ANGSTROMS</u>
MgCO ₃ ·3H ₂ O	6.49	MgSO ₄ ·2H ₂ O	2.03, 4.39
MgSO ₄ ·7H ₂ O	5.91	MgSO ₃ ·6H ₂ O	2.76
MgSO ₄ ·6H ₂ O	2.89	MgSO ₃ ·3H ₂ O	4.19
MgSO ₄ ·4H ₂ O	3.93, 5.41	MgO	3.04
MgSO ₄ ·3H ₂ O	2.49	Mg(OH) ₂	1.49, 1.57, 1.79, 2.39

The 2.10 angstrom spacing for MgO in the freshly processed NelSorbent disappears on flue-gas exposure but reappears on regeneration. Some residual MgSO₄ is present under all methods of regeneration. Several unidentified spacings were found when the NelSorbent was regenerated in CH₄/N₂ but disappeared when the material was reheated in air. Any sulfides, for example, would be oxidized to the sulfate and/or the oxide in air.

NelSorbent exposed to superheated steam and NO_x in the laboratory developed a red-orange color. X-Ray spacings showed MgO, Mg(OH)₂ and Mg(NO₃)₂. The nitrate occurred at 3.34 angstroms and was not found in any flue gas exposed samples of NelSorbent.

Electron Micrographs

At 100,000 magnifications of the NelSorbent, the MgO or Mg(OH)₂ patches were observed to be sparsely but uniformly distributed on the vermiculite. As the magnification increased, the patches appeared as crystalline clusters with a high degree of porosity. At the highest magnification, the clusters seemed to be composed of needles several hundred nanometers in length and about 50 nanometers in cross-section.

SUMMARY

The surface area of the NelSorbenents is larger than would be expected from the collective surface areas of the constituent vermiculite and MgO suggesting that the vermiculite support is enhancing surface area development of the MgO. There is evidence of a mesoporous structure in the NelSorbent from the electron micrographs and by the hysteresis of some of the desorption isotherms. Difficulty in establishing baseline weights of the NelSorbenents also suggests the existence of a microporous structure. MgO is a better starting material than either Mg(OH)₂ or MgCO₃ for preparation of the NelSorbent. The carbonate does not seem to completely decompose in the conditioning process.

There is a loss of surface area when the NelSorbenents are subjected to too high a temperature. This can happen during conditioning or regeneration or when hot spots develop in batch conditioning or when sieved fractions tend to fuse. The vermiculite basal plane structure can also be collapsed by the higher temperatures.

Sulfites, sulfates, and sulfides are detected by FTIR, X-Ray, or qualitative tests. The sulfite tends to oxidize to the sulfate over longer periods of time. Some sulfate tends to remain even under fairly rigorous regeneration techniques. Any sulfides produced by a reducing regeneration atmosphere are reoxidized to sulfate or oxide by heating in air.

Nitrites or nitrates were not detected in pilot plant NelSorbent samples due to the small concentration of NO_x in the flue-gas. They were variously detected in laboratory treated samples by FTIR, X-Ray, and qualitative tests.

Moisture plays an extremely important role in the adsorption process. Burning wet coal or adding moisture to the sorbent bed increased the adsorption efficiency of the NelSorbent for SO_2 and NO_x . This observation is confirmed by laboratory studies under static conditions. X-Ray studies and adsorption studies with water substantiated the penetration of the vermiculite interlayers.

Dynamic studies have shown larger percentage utilizations of the NelSorbents than have static studies in the laboratory. Future studies will need to address what factors in the dynamic systems are responsible for this difference.

ACKNOWLEDGMENT

This work was funded by a Thomas Edison Seed Grant from the state of Ohio. The space for the pilot-plant operations was donated by the Ohio Edison Company.

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Key Words: sorption, flue-gas, vermiculite

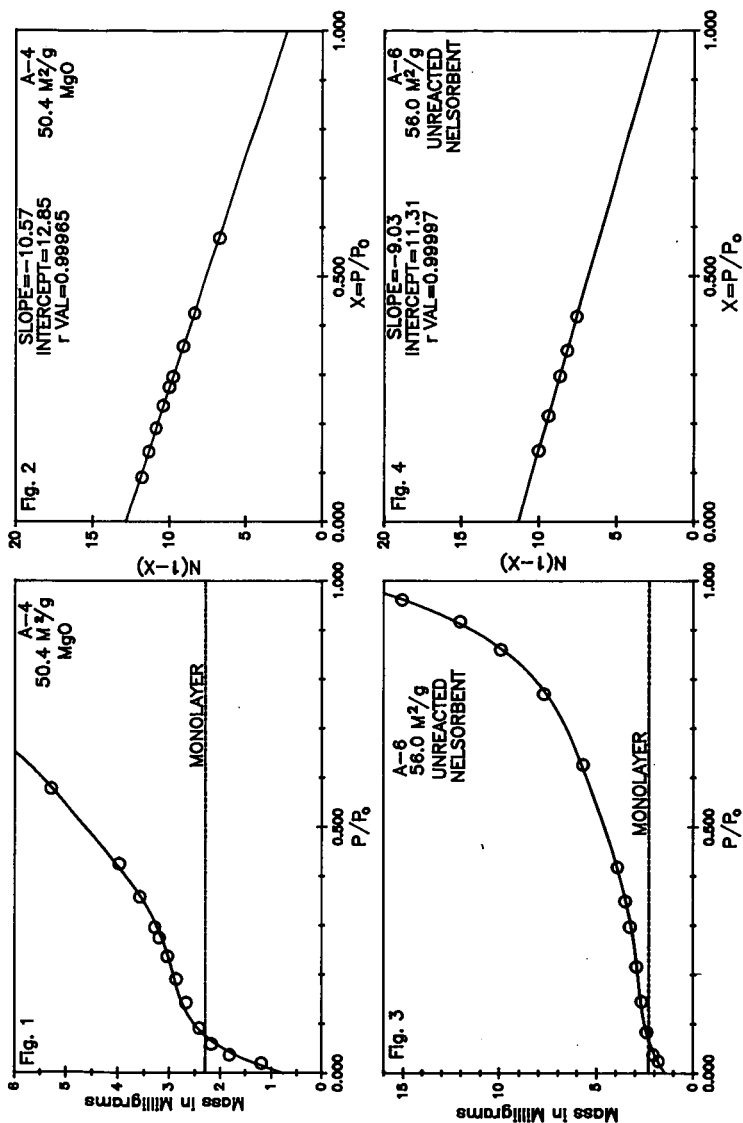


Figure 1 - Adsorption isotherm of MgO processed at 550°C.
 Figure 2 - Variation of BET plot to determine mass of A-4 monolayer.
 Figure 3 - Adsorption isotherm of Nelsorbent processed at 550°C.
 Figure 4 - Variation of BET plot to determine mass of A-6 monolayer.